UNIT THREE

CHAPTER 6

CERAMICS AND ITS PROPERTIES

Introduction

Ceramics are nonmetallic inorganic substances, which are brittle and have good thermal and electrical insulating properties. Most ceramics are compounds between metallic elements and nonmetallic elements for which the interatomic bonds are predominantly ionic but having some covalent character. The term ceramic comes from the Greek word keramikos which means "burnt stuff" indicating that desirable properties of these materials are normally achieved through a high temperature heat treatment process called firing.

Human have found applications for ceramics for the past 30,000 years. Every day new and different applications are being discovered. This truly makes ceramics a stone age material with space age qualities. Ceramics can be divided into two classes: traditional and modern. Ceramics the primary raw material is clay is considered to be traditional. Some traditional ceramics are

1. Porcelain

It is developed in China. Heating a clay mineral known as Kaolin in a kiln, a type of oven. It is strong, hard durable and resistant to chemicals, heat and thermal shock. Combines well with glazes and paints. porcelain is a white material that provides an excellent base for decorative pottery and art much like white paper porcelain was an expensive material that was considered as the most prestigious form of pottery. It is still used today for premium table ware and decorative items. Porcelain is also used as an electric

insulating material in equipments such as power transformers and in construction components such as bathroom fixtures.

2. Bone china

It is exclusively produced in U.K. It is a type of porcelain made with bone as a key ingredient. It is considered as premium material due to its history of being manufactured in U.K to produce high quality tableware and ornamental items.

3. Earthenware

It is made with selected clays and other materials and is not heated to the point of vitrification that gives porcelain and other ceramics their glassy, translucent and nonporus properties. Earthenware is opaque, porus and is softer than porcelain.

It has low mechanical strength and can easily chipped and scratched. Requires less energy to produce than most other ceramics and is relatively inexpensive. An opaque colour that is often similar to clay with browns, reds and oranges being common. Earthenware must be glazed to be watertight. It is used to make inexpensive tiles and pottery such as flower pots.

4. Stoneware

Stoneware is fired at a temperature above earthenware but below porcelain. This results in a vitreous or semivitreous ceramic that is watertight but not as translucent and white as porcelain.

Stoneware is often valued for its earthy look and relative strength as compared to earthenware. Its properties are similar to porcelain apart from its appearance. Stoneware is used to make both expensive and inexpensive pottery and tiles.

5. Glass ceramics

A ceramic produced with a process of controlled crystallization that has properties similar to glass with the strength and durability of ceramics. Glass ceramics are created with advanced manufacturing processes that produce materials with desirable traits such as high mechanical strength, zero porosity, durability, translucency, low thermal expansion, high temperature stability, high chemical durability, biocompatiability and superconductivity.

It is used to make cooktops, cookware, bakeware medicinal devices, scientific and industrial equipment.

6. Fired bricks

Bricks produced by heating minerals such as sand and clay are ceramics.

In general they are durable, heavy, brittle and can withstand high temperatures. It is used to make walls, landscaping, fire places and chimneys.

Note: Silicon is a ceramic material due to its chemical properties. Silicate materials are extremely abundant as they make up about 90% of the Earth's crust. Clays and sand that are used to create common ceramics are silicon based. For example, the kaolinite used to make porcelain and the silica used to make fired bricks are silicate materials.

After significant progress has been made in understanding the fundamental character of these materials and of the phenomena that occur in them that are responsible for their unique properties a new generation of these materials has evolved and termed as modern ceramics or simply ceramics.

On the basis of their applications ceramics materials divided into six. They are (1) glasses (2) clay products (3) refractories (4) abrasives (5) cements and (6) advanced ceramics. Further the glasses are subdivided into two: glasses and glass ceramics. Clay products are subdivided into two: structural clay products, refractories are subdivided into four: fire clay, silica, basic and special. The classification is shown in figure 6.1.

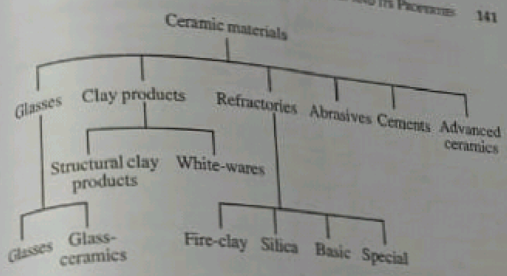


Figure 6.1: Classification of ceramic materials on the basis of application

Now we discuss each ceramic material one by one.

Glasses

Glasses come under the general name ceramics. Glasses are noncrystalline silicates (SiO_2) containing small amount of other oxides such as Na_2O (soda), CaO (Lime), Al_2O_3, B_2O_3, K_2O, MgO, TiO_2 and Al_2O_3. The addition of oxides influences the properties of glass. Some familiar glasses are soda lime glass, Borosil glass, crown glass, flint glass, fibre glass etc. A typical sodalimeglass consists of about 74 mass % of SiO_2, 16 mass % Na_2O, 5 mass % CaO and 1 mass % Al_2O_3. The compositions of several common glass materials and their characteristics and uses are given in table 6.1. Glasses are relatively easy to make and are optically transparent. They are used as containers, lenses, fibreglass etc.

Table 6.1: Compositions and characteristics of some glasses

Glass type	Composition (Mass %)						Characteristics and applications
	SiO_2	Na_2O	CaO	Al_2O_3	B_2O_3	Other	
Fused silica	>99.5						High melting temperature, very low coefficient of expansion (thermally shock resistant)
96% Silica (Vycor)	96				4		Thermally shock and chemically resistant – laboratory ware
Borosilicate (Pyrex)	81	3.5		2.5	13		Termally shock and chemically resistant – ovenware
Container (soda-lime)	74	16	5	1		4MgO	Low melting temperature, easily worked also durable
Fibre glass	55		16	15	10	4MgO	Easily drawn into fibres – glass resin composites
Optical flint	54	1				37PbO, $8K_2O$	High density and high index of refraction – optical lenses
Glass-ceramic (Pyroceram)	43.5	14		30	5.5	$6.5TiO_2$, $0.5As_2O_3$	Easily fabricated, strong; resists thermal shock – ovenware

Glass-Ceramics

Glass-ceramics are fine grained polycrystalline material.

Glass-ceramics are made from noncrystalline glasses by subjecting it to proper high temperature heat treatment called crystallization. It is due to crystallization small glass ceramic grains are produced. The transformation from noncrystalline state to crystalline state is a phase transformation. To promote crystallization process usually titanium dioxide is added in the glass during heat treatment.

Characteristics

1. They have high mechanical strengths
2. Low coefficients of thermal expansion which avoids thermal shock.
3. Able to withstand relatively high temperatures.
4. Good dielectric properties.
5. Glass ceramics are made optically transparent or opaque.
6. Easy to fabricate.

Uses

1. Glass-ceramics are manufactured commercially under the trade names of Pyroceram, Corningware, Cercor and Vision. The most common uses for these materials are as ovenware tableware, ovenwindows and range tops. This is possible because of their strength, high temperature withstand capability and its resistance to thermal shock.
2. They are used for electronic packaging because of their good dielectric property.
3. In printed circuit boards glass-ceramics are used as substrates and as electrical insulators.
4. Used for architectural cladding and for heat exchangers and regenerators.

Clay products

One of the most important ceramic raw materials is clay. When clay is mixed with water in the proper proportions, we get a plastic mass that is very amenable to shaping. The formed piece is dried to remove some of the moisture. After that it is fired at an elevated temperature to improve its mechanical strength. We get clay products. Clay products are broadly classified into two: the structural clay products and the whitewares. Structural clay products include building brick, paving brick, terra-cotta facing tile, roofing tile and drainage pipe.

Whiteware is any of a broad class of ceramic products that are white to off-white in appearance and contains a significant vitreous and glass component.

Clay is the most important of the ingredients of making whitewares. The clay used in whiteware products is kaolin also known as china clay from which a white, translucent vitreous ceramic can be made. It can be fired at high temperatures without deforming. It imparts whiteness to the finished ware. Kaolin is formed principally from the mineral kaolinite, a hydrous aluminosilicate with a fine, platy structure china clays are composed of mostly of well ordered kaolinite with no impurities. Lower grade whitewares are usually made of ball clalys which contains ordered and disordered kaolinite plus other clay minerals and impurities. These impurities particularly iron oxides render the fired ware off-white to gray or tan in colour.

Whitewares include porcelain, pottery, tableware, china and sanitary ware.

Refractories

Refractories is one of the classes of ceramics which is resistant to decomposition by heat, pressure and chemical attack and retains strength and form at high temperatures. Refractories are polycrystalline, polyphase, inorganic, nonmetallic, porus and heterogeneous. They are composed of oxides or carbides, nitrides etc. of the following materials: silicon, aluminium, magnesium, calcium, boron, chromium and zirconium.

Refractory materials are used in furnaces, kilns, incinerators and reactors. They are also used to make crucibles and moulds for casting glass and metals. Depending upon the composition of materials in refractory ceramic their performance vary. Based on this refractory material is classified into four namely fireclay, silica, basic and special refractories.

Fireclay refractories

The primary ingredients for the fireclay refractories are high purity fireclays. It has mainly two components namely Al_2O_3 and SiO_2. 25 to 45 mass % alumina and 75 to 55 mass % of silica. The manufacturing process involves four steps, raw material processing, forming, firing and final processing. The resulting product can withstand high temperature up to 1587°C. Upgrading the alumina content will increase the maximum withstand temperature.

They are used to make fire clay bricks used in furnace construction to confine hot atmospheres and to thermally insulate structural members from excessive temperatures. For fireclay bricks strength is not important because suppon of structural loads is not usually required.

Silica refractories

It is also called as acid refractories. The prime ingredient of silica refractories is silica. Silica materials can withstand high temperature. They are used in the arch roofs of steel and glass making furnaces. They are also used as containment vessels because they are resistant to slags that are rich in silica.

Basic refractories

The refractories that are rich in periclase or magnesia (MgO) are termed basic. They may also contain calcium, chromium and iron compounds. The presence of silica adversely affect their high temperature performance. Basic refractories are especially resistant to attack by slags containing high concentrations of MgO and CaO and find extensive use in some steel making hearth furnaces.

Special refractories

High purity oxide materials such as Al_2O_3, SiO_2, MgO, BeO, ZrO_2 which are having little porosity are special refractories. Carbon, graphite and siliconcarbide are also special refractories. Siliconcarbide has been used for electrical resistance heating elements, as a crucible material and in internal furnace components. Though carbon and graphite are very refractory but find limited application because they are susceptible to oxidation in excess of about 800°C.

Abrasives

Abrasives are ceramic materials, often minerals, that is used to shape or finish a work piece through rubbing, which leads to part of the work piece to worn away by friction. While finishing a material often means polishing it to gain a smooth, reflective surface, the process can also involve roughening as in satin or beaded finishes. In short the ceramics which are used to cut, grind and polish other softer materials are known as abrasives.

Abrasives are hard, tough and are not easily fracture.

Diamonds both natural and synthetic are used as abrasives. However they are relatively expensive. The more common ceramic abrasives are silicon carbide, tungsten carbide, aluminium oxide and silica sand. These are used in a wide variety of industrial, domestic and technological applications.

In grinding wheels abrasives are coated by means of an organic resin. Another example we are familiar with sand paper. Here abrasives (sands) are coated on special type of paper or cloth material. This is used to polish wood, metals and other ceramics.

Cements

Cement, plaster of paris and lime come under a group ceramics and classified as inorganic cements. When these materials is mixed with water, they form a paste that subsequently sets and hardens. It is useful in the construction of solid and rigid structures in any shape. When mixed with water chemical reaction takes place and they become a single cohesive structure. Unlike refractory materials, cements create strong chemical bonding at room temperature.

Of this group of materials portland cement is extensively used. It is produced by grinding and intimately mixing clay and lime bearing minerals in the proper proportions and then heating the mixture to about 1400°C in a rotary kiln. This process is called calcination. This produces physical and chemical changes in the raw materials. The resulting product called clinker is then ~~ground~~ grind into a very fine powder to which a small amount of gypsum

($CaSO_4 \cdot 2H_2O$) to retard the setting process. This product is portland cement. The properties of portland cement including setting time and strength depends on its composition.

Several different constituents are found in portland cement. Two of them are tricalcium silicate ($3CaO \cdot SiO_2$) and the other one is dicalcium silicate ($2CaO \cdot SiO_2$).

When water is added to portland cement hydration reaction begins, the hydrated products are in the form of gels that form the cementitious bond. These are first manifested as setting which takes places soon after mixing, usually within several hours. Hardening of the mass follows as a result of further hydration, a relatively slow process that may continue for long years. It may be noted that the process by which cement hardens is not one of drying but further hydration process which water actually participates in a chemical bonding reaction.

Portland cement is also called as hydraulic cement because its hardness develops by chemical reaction with water. Other cement materials such as lime are nonhydraulic because compounds other than water such as CO_2 are involved in the hardening process.

Advanced ceramics

The term advanced ceramics refers to all the products made from inorganic, high purity compounds through a series of specialised manufacturing processes.

Alumina, aluminium nitride, zirconia, silicon carbide, silicon nitride and titanium based materials are examples of advanced ceramics.

Advanced ceramics can be used for purposes due to their permeability, electric and magnetic properties, insulation, conduction, etc. Furthermore advanced ceramics are utilised in optical fibre communications systems, in microelectro mechanical systems (MEMS), as ball bearings, and in applications that exploit the piezoelectric behaviour of a number of ceramic metals. We will discuss optical fibres, ceramic ball bearings and piezoelectric ceramics.

Optical fibres

Optical fibre is a new and advanced ceramic material that is used in our modern communication systems. The optical fibre is made of extremely high purity silica, which must be free of even minute levels of contaminants and other defects that absorb, scatter and attenuate a light beam. Very advanced and sophisticated processing techniques have been developed to produce fibres that meet the rigid restrictions required for this application.

Ceramic ball bearings

Another important application of advanced ceramic material is in ball bearings. A bearing consists of balls and races that are in contact with rub against one another when in use. In the past both ball and race components have been made of bearing steels that are very hard, extremely corrosion resistant and may be polished to a very smooth surface finish over past decade or so silicon nitride (Si_3N_4) balls have begun replacing steel balls in a number of applications, since several properties of Si_3N_4 make it a more desirable material. In most instances races are still made of steel, because its tensile strength is superior to that of silicon nitride. This combination of ceramic balls and steel races is termed hybrid bearing.

Advantages of ceramic ball bearings over traditional ball bearings

1. The hybrid ball bearing weighs less than the conventional ball bearing. This is because the density of Si_3N_4 (3.2 gcm^{-3}) is less than steel (7.8 gcm^{-3}).
2. The centrifugal loading is less in the hybrids because of its small mass; as a result they may operate at higher speeds (about 20% - 40% more).

3. The Si_3N_4 balls are more rigid than steel balls since the modulus of elasticity of Si_3N_4 is higher. Because of this Si_3N_4 undergoes lower deformation.
4. Since Si_3N_4 is harder than steel its lifetime is longer.
5. Silicon nitrides have superior strength than steel, silicon nitride undergoes lower wear rates.
6. Since the coefficient of friction of Si_3N_4 is 30% that of steel, Si_3N_4 produces less heat due to friction. This increases the grease life.
7. Ceramic materials are more corrosion resistant than metal alloys, the silicon nitride balls may be used in more corrosive environments and at higher operating temperatures.
8. Si_3N_4 is an insulator and steel is a conductor. Because of this ceramic bearing are immune to arcing damage. spark

Uses of ceramic bearings

1. The hybrid bearings are used in line skates bicycles, electric motors, machine tool spindles, precision medical hand tools.
2. They are used in textile. industry
3. Used for food processing and also for chemical equipments.

However there are some challenges in making the silicon nitride bearing material. They are

1. processing technique to yield a pore-free material.
2. fabrication of spherical pieces that require minimum of machining.
3. polishing technique to produce a smoother surface finish than steel balls.

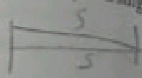
Piezoelectric ceramics

Some ceramic materials exhibit the phenomenon of piezoelectricity. **When a material is subjected to a mechanical strain an electric field (voltage) is developed in the material.**

This phenomenon is called piezoelectric effect. The inverse piezo electric is also displayed by these materials. When a material is subjected to an electric field (voltage), a mechanical strain is developed in the material called inverse piezoelectric effect.

Piezoelectric materials may be used as transducers between electrical mechanical energies. A transducer is a device converts variations in pressure into an electrical signal or vice versa. One of the uses of piezoelectric ceramics was in SONAR. SONAR stands for sound navigation and ranging. It works on the principle of reflection method. Here ultrasonic waves are sent through ocean from a transmitter. These waves get reflected back from the objects such as rock, submarine in their path, if any. The reflected waves travel back and received by the detector. Note the time difference between the transmitting wave and the receiving wave say t. Using the formula

$$\text{distance} = \text{speed} \times \text{time}$$



$$2s = vt \text{ or } s = \frac{vt}{2}$$

knowing v, the speed of sound wave the distance s can be calculated.

A piezoelectric crystal is caused to oscillate by an electric signal, which produces high frequency mechanical vibrations that are transmitted through ocean. Upon encountering an object, these signals are reflected back and another piezoelectric material receives this reflected vibrational energy, which it then converts back into an electrical signal. Distance from the ultrasonic source and reflecting body is determined from the elapsed time between sending and receiving signals.

Other applications of that used piezoelectric devices are found in automotive, computer and medical sectors. Some of these applications are automotive wheel balances, seat belt buzzers, tread-wear indications keyless door entry and airbag sensors in vehicles.

They are also used in computers as microactuators for hard disks and notebook transformers, in ink-jet printing heads, ultrasonic welders and smoke detectors. In medical field they are used in insulin pumps, ultrasonic therapy and in ultrasonic cataract removal devices.

Commonly used piezoelectric ceramics are barium titanate, lead titanate, lead zirconate-titanate and potassium niobate.

Stress-strain behaviour of materials

Breaking strength of a material

Breaking strength is the ability of a material to withstand load. It is measured in force per unit area, i.e. stress (σ).

$$\sigma = \frac{F}{A} \qquad \text{---(1)}$$

Its unit is pascal (Nm^{-2}). Higher units MPa (10^6 Pa) or GPa (10^{12} Pa) are used to measure stress.

There are three ways in which the load may be applied namely

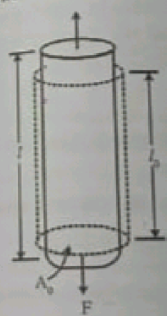


Figure 6.2(a)

Schematic illustration of how a tensile load produces an elongation and positive linear strain. Dashed lines represent the shape before deformation; solid lines, after deformation

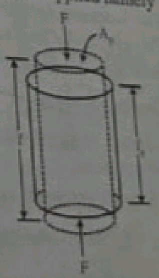


Figure 6.2(b)

Schematic illustration of how a compressive load produces contraction and a negative linear strain

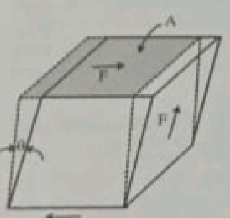


Figure 6.2(c)

Schematic representation of shear strain γ, where $\gamma = \tan\theta$

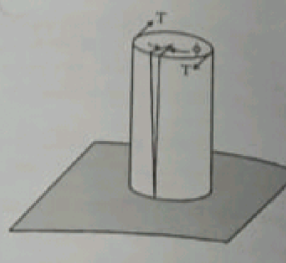


Figure 6.2(d)

Schematic representation of torsional deformation (i.e., angle of twist ϕ) produced by an applied torque T.

tension, compression or shear. See the figure 6.2 (a, b and c). Many loads produce torsion rather than shear. It is depicted in 6.2 (d). Corresponding to each load there exist a breaking stress. If the load is tension the corresponding breaking stress is called tensile strength. If the load produces compression the corresponding breaking stress is called compressive strength and so on.

Tensile strength

Tensile strength indicates the resistance of a material to breaking under tension.

Tensile strength is measured as the maximum stress $\left(\sigma_m = \frac{F}{A}\right)$ that a material can support without fracture

To study the mechanical behaviour of a material we perform stress-strain test.

If a load is static or changes slowly with time and is applied uniformly over a cross section, the mechanical behaviour of the material may be ascertained by a simple stress-strain test. One of

the most important common mechanical stress-strain tests is performed in tension called tension test.

Tension test

This test is performed to find the breaking stress of metallic materials. The test is performed as follows. A specimen material is subjected to a gradually increasing tensile load that is applied uniaxially along the long axis of the specimen. A standard tensile specimen is shown in figure 6.3. Normally the cross of the specimen is circular, but rectangular specimens are also used. This specimen configuration was chosen so that, during testing, deformation is confined to the narrow centre region and also to reduce the likelihood of fracture at the ends of the specimen.

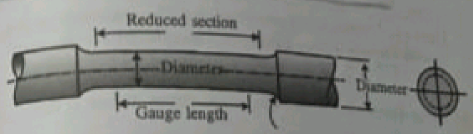


Figure 6.3: A standard tensile specimen with circular cross section

The specimen is mounted by its ends into the holding grips of the testing apparatus (see figure 6.4). The tensile testing machine is designed to elongate the specimen at a constant rate.

Note down the instantaneous applied loads and the corresponding elongations. Continue the process till the specimen is permanently deformed and usually fractured. The output of such a tensile test is recorded as load versus elongation.

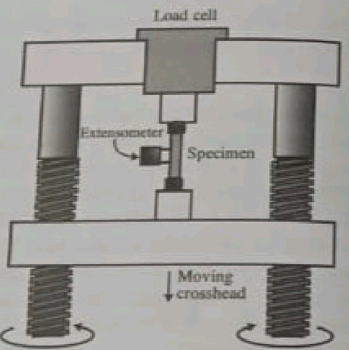


Figure 6.4: Schematic representation of the apparatus used to conduct tensile stress-strain tests. The specimen is elongated by the moving crosshead

From these observations we can draw stress-strain graph

$$\text{stress,} \quad \sigma = \frac{F}{A} \qquad \text{..... (2)}$$

$$\text{strain,} \quad \varepsilon = \frac{\Delta l}{l} \qquad \text{..... (3)}$$

From the graph we can find out the tensile breaking strength along with other several useful informations.

Stress-strain behaviour of ceramics

Flexural strength

The stress-strain behaviour of brittle ceramics cannot be understood by a tensile test because of three reasons.

1. It is difficult to prepare test specimens having the required property.

2. It is difficult to grip brittle materials without fracturing them.
3. Ceramics fail after only about 0.1% strain, which necessitates that tensile specimens be perfectly aligned to avoid the bending stresses, which are not easily calculated.

To overcome these difficulties we go for measuring its flexural strength. Flexure meaning the action of bending.

Flexural strength also known as modulus of rupture or bend strength or transverse rapture strength is a material property defined as the stress in a material just before it yields in a flexure test.

OR

Flexural strength is the ability of the material to withstand bending forces applied perpendicular to its longitudinal axis.

The transverse bending test is most frequently employed in which a specimen having either a circular or rectangular cross section is bent until fracture using a three point flexural test technique.

For a rectangular sample under load in a three point bending set up is shown in figure 6.5.

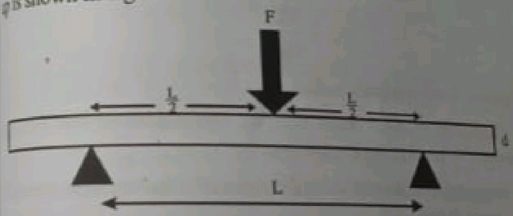
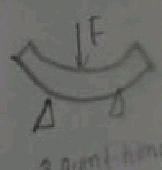


Figure 6.5



By definition

Flexural strength,

$$\sigma_{fs} = \text{stress} = \frac{Mc}{I}$$

where M is the maximum bending moment, c is the distance from the centre of specimen and I is the geometrical moment of inertia.

For rectangular specimen

$$M = \frac{FL}{4}, \quad c = \frac{d}{2}$$

$$I = \frac{bd^3}{12},$$

where b is the breadth and distance thickness of the specimen.

$$\therefore \qquad \sigma_{fs} = \frac{3FL}{2bd^2} \qquad \text{..... (4)}$$

Similarly for circular cross section

$$M = \frac{FL}{4}, \quad c = R$$

$$I = \frac{\pi R^4}{4}$$

$$\therefore \qquad \sigma_{fs} = \frac{FL}{\pi R^3} \qquad \text{..... (5)}$$

where R is the specimen radius.

Equations 4 and 5 show that we can calculate the flexural strength by conducting flexure test.

Characteristic flexural strength values of some ceramic materials are given in table 6.2.

$$\frac{\frac{FL\,l}{4}}{bd^3} = \frac{\frac{FC}{2}\,d/2}{\frac{bd^3}{12}}$$

Table 6.2: Flexural strength and modulus of elasticity

Material	*Flexural Strength (MPa)*	*Modulus of Elasticity (GPa)*
Silicon nitride (Si_3N_4)	250-1000	304
Zirconia (ZrO_2)	800-1500	205
Silicon carbide (SiC)	100-820	345
Aluminum oxide (Al_2O_3)	275-700	393
Glass-ceramic (Pyroceram)	247	120
Mullite ($3Al_2O_3$-$2SiO_2$)	185	145
Spinel ($MgAl_2O_4$)	110-245	260
Magnesium oxide (MgO)	105	225
Fused silica (SiO_2)	110	73
Soda-lime glass	69	69

Elastic behaviour

From the data available from the flexure test we obtain several values of strain and stress. Using these draw a graph between strain on the horizontal axis and stress on the vertical axis. This gives us the elastic stress-strain behaviour of ceramic material.

Since $\frac{\text{stress}}{\text{strain}}$ gives modulus of elasticity, it is given by the slope of the stress-strain graph.

From the graph is seen that stress and strain relationship is linear which is analogous to tensile test results for metals. A typical stress-strain behaviour to fracture for aluminium oxide and glass are given in figure 6.6 for comparison. The corresponding breaking is marked as (x) in the figure. From the graph it can also be noted that neither material experiences plastic deformation prior to fracture.

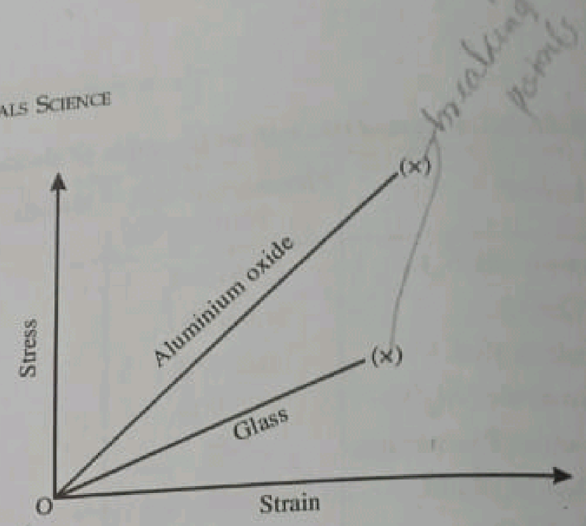


Figure 6.6: Stress-strain behaviour

Modulus of elasticity for several ceramic materials are also given in table 6.2.

UNIVERSITY MODEL QUESTIONS

Section A

(Answer questions in two or three sentences)

Short answer questions

1. What is meant by firing process?
2. Why new ceramics are termed as stone age material with space age qualities?
3. Classify ceramics.
4. What is porcelain?
5. What is bone china?
6. What are the uses of porcelain?
7. What are the uses of earthenware?
8. What is stoneware?
9. What are the uses of stoneware?
10. What is glass ceramics?

11. What are th
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